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Recent scenario and technologies to utilize non-edible oils for biodiesel production

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ABSTRACT

It is well known that energy consumption is rapidly increasing due to population growth, higher standard of living and increased production. Significant amounts of energy resources are being consumed by the transportation sector leading to the fast depletion of fossil fuels and environmental pollution. Biodiesel is one of the technically and economically feasible options to tackle the aforesaid problems. Biodiesel is produced mainly from edible oils. However, it is believed that the extensive use of edible oils for biodiesel production may lead to food shortages in most of the developing countries. Therefore, the aim of this paper is to review the necessity and potentiality of the non-edible oils and to identify the emerging technologies to produce biodiesel. Special attention has been paid to the impact of biofuels on agricultural commodity prices and the food–fuel debate.

Contents

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1. Introduction

It is well known that a considerable amount of biodiesel is produced from edible oils [1]. However, the extensive use of edible oils might lead to some negative impacts such as starvation and higher food prices in developing countries [2]. For instance, in Malaysia the biodiesel refineries have created shortages in palm oil. Therefore the price of palm oil for cooking has risen by 70% [3]. The rising food prices may be beneficial to the poor farm producers but at the same time they are unlikely to benefit the urban poor [4]. Some researchers have pointed out that developing the technology to convert cellulosic materials into biofuels will significantly reduce food shortage problems [5]. In addition to this, the waste edible oil may be made primary feedstock and the fresh edible and non-edible oils should be made supplement feedstocks. This may reduce the food shortages significantly [6]. However, many of the researchers agree that non-edible oils are the suitable alternative to edible oils for biodiesel production. Hence, the recent focus is to find non-edible oil feedstocks for biodiesel production [7].

Many of the reviewing papers have tried to report the necessity and feasibility of non-edible oils for biodiesel production. A lot of work is being carried out on biodiesel production from Jatropha oil in countries like India, Malaysia and Indonesia [8–12].

However, recent trends and technologies for the production of biodiesel from non-edible oils and the impact of price rise of the food commodities due to the consumption of edible oils for biodiesel have not yet attracted the attention they deserve.

The aim of this paper is to emphasize the effects of food shortages due to the consumption of edible oils and to present the different potentials of non-edible feedstocks for biodiesel production. Special attention has been paid to established processes and considerations for emerging technologies of potential interests.

2. International trends in food demand and supply

There are concerns regarding whether a growing population can be fed in a sustainable manner or not [13]. When dwarfism was introduced in wheat and rice, yields were raised by 2–3% per year during two to three decades [14]. The Malthusian prognosis has been undermined by an exponential increase in world food supply, mainly maize, rice and wheat since 1960 [15]. The development of innovative technologies resulted in both improved genetic traits and advanced crop management. Despite these trends a decline of rice yields from 1985 onwards has been reported for the Indo-Gangetic Plains in India [16]. In spite of these variations in the yield of different crops, there is still a gap between the growth of production and demand of supply. Additionally, there may be other factors but the demand of edible feedstocks for biofuel cannot be ruled out.

3. Food for poor or fuel for rich – a debate

There are many factors which cause the increase in food commodity prices [17]. It is difficult or impossible to separate the reasons responsible for the increase of commodity price other than biofuels. As far as biofuels are concerned, it is argued that one must distinguish between biofuels driven by market forces and biofuels driven by government policy [18]. However, it is accepted globally that biofuels produced from edible feedstocks cannot replace the petroleum fuels without impacting food supplies [19].

4. Effects of elevated food prices on poverty

It has been reported by many researchers and non-governmental organizations that higher food commodity prices adversely affect the poor in general and urban poor in particular. The urban poor in many countries spend a much higher percentage of their income on food [20,21]. The reason for their argument is the production of biofuels. Therefore, for the researchers and scientists the challenge is to produce enough food and biofuel for people in an environmentally sound manner.

5. Biodiesel

Biodiesel is a renewable and clean burning combustible fuel for diesel engines [22]. It is nontoxic, biodegradable, and virtually free from aromatics and sulfur contents [23]. This is because its primary components are domestic renewable resources such as vegetable oil and animal fats consisting of long-chain alkyl (methyl, ethyl, or propyl) esters [24]. Biodiesel is the mono-alkyl esters of fatty acids that result from animal fats or vegetable oils [25]. In other words, biodiesel (fatty acid ester) is the end result of the chemical reaction caused by mixing vegetable oil or animal fat with an alcohol such as methanol. Together these ingredients produce a compound recognized as a fatty acid alkyl ester. A catalyst such as sodium hydroxide is also necessary in order for the biodiesel to be considered a finished product, and is added with the new compounds to produce biodiesel.

Biodiesel offers many advantages as it is [26–30]

- renewable and energy efficient;
- usable in most diesel engines with no or only minor modifications;
- nontoxic, biodegradable and suitable for sensitive environments and
- a fuel with high flash point, positive energy balance and reduced emissions of carbon monoxide (CO), total hydrocarbon (THC) and particulate matter (PM).

Apart from the above advantages, following are the disadvantages of biodiesel: [31,32]

- Biodiesel has 12% lower energy content than diesel.
- Due to the high oxygen content in biodiesel, it produces relatively higher NO_x.
- Biodiesel can cause corrosion in vehicle material.

5.1. Production technologies

The high viscosity, low volatility and polyunsaturated characteristics of vegetable oils make them unsuitable to be used in

diesel engines. These problems could be solved to an extent by methods like pyrolysis, dilution (direct blending), micro-emulsion, and transesterification. Dilution and micro-emulsion processes are not preferred due to higher viscosity and bad volatility though they are simple [33]. Pyrolysis process is found to be simple and environment friendly [34]. However, the transesterification process is commonly used for the production of biodiesel. Transesterification is the reaction of a fat or oil with an alcohol commonly methanol to form its methyl esters and glycerol. To improve the reaction rate and yield, usually sodium hydroxide or potassium hydroxide is used as catalyst. Fig. 1 shows the different processes employed for biodiesel production.

Generally, there are two types of transesterification processes. They are catalytic and non-catalytic transesterification. Transesterification reaction can be catalyzed by both homogeneous (alkalis and acids) and heterogeneous catalysts. Homogeneous catalysts are better in performance when the free fatty acid content in the crude oil is $<1\%$ [35]. The expensive separation of catalyst from the mixture and formation of the unwanted by-product (soap) are the limitations of the homogenous catalyst [36].

The performance of heterogeneous catalysts is found better for the transesterification reaction of vegetable oils when their free fatty acid (FFA) content is $>1\%$. The separation of catalyst from the reaction products is easier than the homogenous catalysts. However, for the transesterification process for biodiesel production both types of catalyst methods have been found to be suitable [24,37].

In general, the catalyst increases the reaction rate of the transesterification and also enhances the solubility of alcohol as well. Acid-catalyzed reaction is used to reduce the higher acid value of the feedstocks, as a pretreatment step known as esterification. However, the reaction rate is relatively slower than with transesterification [38]. A higher conversion could be achieved by increasing the reaction temperature and the reaction time [39,40].

Base-catalyzed reaction is faster than the acid-catalyzed reaction but the yield of biodiesel is lowered due to the formation of soap. In addition to this, the separation of biodiesel from glycerol is quite difficult. However, it is observed that methoxide catalysts give higher yields than hydroxide catalysts [41].

The other methods such as supercritical processes, microwave and ultrasonic irradiation systems are also being used but to a lesser extent. The conventional methods of transesterification with yield and the reaction conditions employed for some non-edible oils have been shown in Table 1.

5.2. Limitations of existing production technologies

Generally non-edible feedstocks including waste vegetable oils, animal fats and non-food crops are produced by conventional transesterification reaction. However, owing to the limitations of the conventional methods new technologies are starting to be developed. In the previous chapters it was pointed out that biodiesel could be produced by different technological processes, mainly transesterification using homogeneous catalysts as well as heterogeneous catalysts. All these available methods are capable of producing biodiesel from refined oil [66] which is the most common source of raw material for its production. However, they have their own advantages and disadvantages [67].

The acid-catalyzed homogeneous transesterification has not been widely investigated and employed compared to the alkali-catalyzed process due to its limitations such as slower reaction rates, the need for tougher conditions (higher temperatures, methanol-to-oil molar ratios and quantities of catalysts) and the formation of undesired secondary products such as dialkyl or glycerol ethers. Therefore it is less attractive to the industrial purposes [68]. On the other hand, the main problem associated with the heterogeneously catalyzed transesterification is the deactivation due to the presence of water, which is normally produced from the esterification reaction [67].

Enzymes are believed to be a good choice to produce biodiesel; they can easily treat fatty acids as well as triglycerides to produce biodiesel from non-edible oils with higher conversions [37]. However, their high production cost limits their employability [69]. This may be overcome by using molecular technologies to enable the production of enzymes in higher quantities as well as in a virtually purified form [70].

The most common and simple non-catalyzed biodiesel production process is by using supercritical methanol. Though the procedure is claimed to be effective, it is highly expensive [68,71]. Hence, there has been more research to explore new technologies for the production of biodiesel considering the economic viability for industrial attraction.

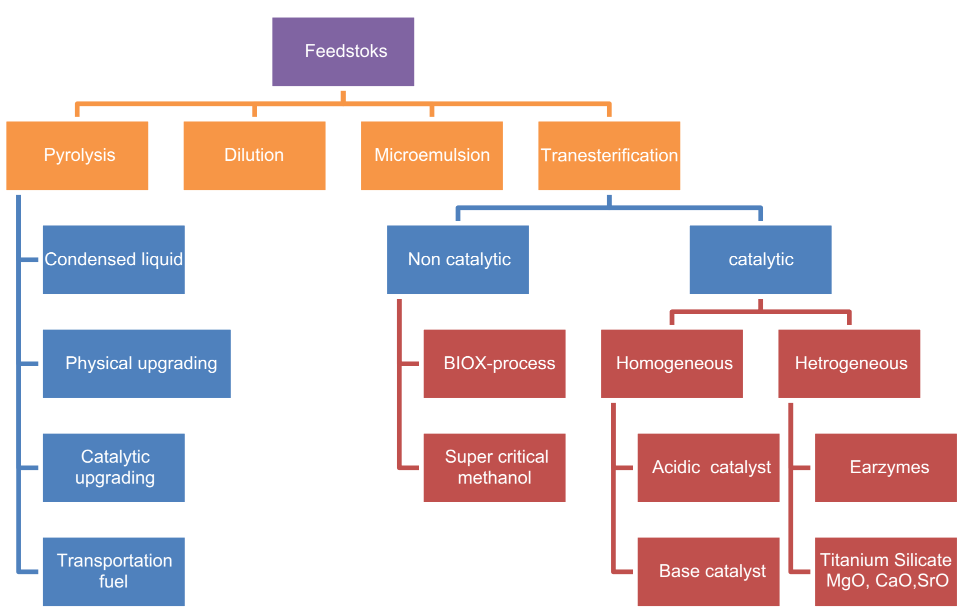

Fig. 1. Methods for biodiesel production [42,43].

Table 1
Conventional methods for biodiesel production.

Transesterification method	Description (oil/acid/base catalyst)	Biodiesel yield (%)	Ref.
Homogeneous catalyzed (acids and base)	Jatropha oil Step 1: Esterification with 1% H_2SO_4 Step 2: Transesterification by 1% NaOH	90.1% at 6 h reaction	[44,45]
	Karanja oil Step 1: Esterification with 1.5% H_2SO_4 Step 2: Transesterification by 0.8% NaOH, 1% CH_3ONa and 1% KOH	90–95% at 2 h reaction	[46]
	Step 1: Esterification with 0.5% H_2SO_4 Step 2: Transesterification by 2% KOH	80–85% at 1.25 h reaction	[47]
	Ceiba pentandra oil Step 1: Esterification with 1.834% H_2SO_4 Step 2: Transesterification by 1% KOH	99.5% at 1.75 h reaction	[48]
Heterogeneous catalyzed (alkalis and acids)	*Moringa oleifera* 3% Sulphated tin oxide (acid catalyst) at 150 °C	84% at 2.5 h reaction	[49]
	Jatropha oil 7.61% Sulfated zirconia loaded on alumina (acid catalyst) at 150 °C	90.32% at 4 h reaction	[50]
	Jatropha oil 2% CaO/Fe_3O_4 (base catalyst) at 70 °C	95% at 80 min 99% at 4 h reaction	[51]
	Jatropha oil 1% Mg–Al hydrotalcites (base catalyst) at 45 °C	95.2% at 1.5 h reaction	[52]
Supercritical processes	Jatropha oil At temperature of 320 °C and pressure of 15 MPa	84.6% at 5 min reaction	[53]
	Krating oil At temperature of 260 °C and pressure of 16 MPa	90.4% at 10 min reaction	[53]
	Jatropha curcas oil Step 1: Sub-critical water treatment at temperature of 270 °C and pressure of 27 MPa for 25 min Step 2: Supercritical dimethyl carbonate treatment at temperature of 300 °C and pressure 9 MPa for 15 min	97% at 40 min reaction	[54]
Microwave-assisted transesterification	*Camelina sativa* oil 1.5% BaO as catalyst with 9:1 methanol oil ratio	94% at 4 min reaction	[55]
	Rice barn oil 0.15–0.18% NaOH as catalyst at 80 °C reaction temperature	98.82% at 20 min reaction	[56]
	Pongamia pinnata 0.5% NaOH or 1.5% KOH as catalyst 60 °C reaction temperature	96% at 5 min reaction	[57]
	Yellow horn oil 1% Heteropolyacid (HPA) as catalyst at 60 °C reaction temperature	96.22% at 10 min reaction	[58]
	Castor oil 15% Cesium phosphotungstate-derived catalyst at 70 °C reaction temperature	90% at 4 h reaction	[59]
Ultrasonic irradiation systems	Tung oil 1% CH_3OH and KOH as catalyst at 20–30 °C reaction temperature with ultrasonic frequency of 25 kHz	91.15% at 30 min reaction	[60]
	Jatropha oil Step 1: 4% H_2SO_4 catalyst used for esterification at 60 °C reaction temperature and power of 210 W Step 2: 1.4% NaOH catalyst used for transesterification at 60 °C reaction temperature and power of 210 W	96.4% at 1.5 h reaction	[61]
Enzyme-catalyzed	Jatropha oil 7% Water, 10% immobilized lipase and temperature of 35 °C	94% at 24 h reaction	[62]
	Pistacia chinensis bge seed oil 20% Water, 7 IU/g of oil and temperature of 37 °C	94% at 60 h reaction	[63]
	Babassu oil (Orbinya sp.) lipase PS with productivity (7 mg of biodiesel/g h) and temperature of	90.93% at 72 h reaction	[64]

Table 1 (*continued*)

Transesterification method	Description (oil/acid/base catalyst)	Biodiesel yield (%)	Ref.
	45 °C		
	Stillingia oil 15% Novozyme 435 with tert-butanol and temperature of 40 °C	89.5% at 10 h reaction	[65]

5.3. Biodiesel from non-edible oils

It is estimated that about 84% of the biodiesel production is obtained globally by rapeseed oil, which happens to be an edible oil. Similarly other edible oils such as sunflower oil, palm oil and soybean oil also contribute substantially [42,72]. Since more than 95% of biodiesel is produced from edible oils, many activists are claiming that it is not only conversion of edible oil into biodiesel but also conversion of food into fuel. Recently, non-governmental organizations and social and environmental activists have started to argue the harmful effects of biodiesel production, not only from edible oils but from non-edible oils as well. They argue that usage of edible oils would lead to food starvation and that of non-edible oils would cause deforestation and destruction of the ecosystem [73–75].

However, to overcome this devastating situation or at least to minimize food shortages, researches have been focused toward production of biodiesel from non-edible feedstocks. Several evergreen trees producing non-edible oils can be cultivated in non-arable land. In fact, many Indian states have decided to reserve a total of 1.72 million hectares of land for the cultivation of Jatropha. Furthermore, small quantities of Jatropha biodiesel are already being used successfully by state public transport buses including the railways.

5.3.1. Non-edible feedstocks for biodiesel production

The demand for biodiesel has increased sharply in recent years. To meet the requirements, edible oils alone are not favorable due to various reasons stated earlier. Under this situation only those resources or feedstocks can be considered which are non-edible and produce oil in appreciable quantity. Following are few non-edible feedstocks.

5.3.1.1. Jatropha curcas L. (Jatropha oil). *Jatropha curcas* is a draught-resistant tree mainly found in Central and South America, South-east Asia, India and Africa [76]. It is a plant with multipurpose uses and considerable potential for biodiesel production [77]. The high free fatty acid contents of the jatropha crude oil could be reduced by esterification. Transesterification of the esterified oil gives yield of jatropha biodiesel above 99% [78]. The biodiesel produced from *Jatropha curcas* L. does have similar properties to that of petroleum diesel [79].

5.3.1.2. Pongamia pinnata (karanja oil). *Pongamia pinnata* is a fast growing leguminous tree with a high potential for oil and growth on marginal land [80]. It is an underutilized plant which grows in many parts of India. Applying dual-step transesterification would result in a yield of 96.6–97% biodiesel [81]. The important fuel properties lie within the limit set by ASTM standards and German biodiesel standards [82]. The large-scale cultivation of the *Pongamia pinnata* could make the non-edible feedstock cheaper for biodiesel production [83].

5.3.1.3. Madhuca indica (mahua). *Madhuca indica* is a non-edible oil with higher free fatty acid contents (19%) available largely in central and northern plains and forests of India [84]. Madhuca has two major species, indica and longifolia. The methyl esters of *Madhuca indica* could be used as fuel for internal combustion engines in place of diesel without any modifications on the engines [85].

5.3.1.4. Michelia champaca. *Michelia champaca* is a tall evergreen tree found in China, Burma and throughout India. It is also known as svarna champa. The seeds of michelia are a rich source of oil (45%). The flowers of the tree possess excellent fragrance and hence are used in perfume industry also. The saponification value (SV), iodine value (IV) and cetane number (CN) of the methyl esters *Michelia champaca* indicate its suitability for biodiesel production [86].

5.3.1.5. Garcinia indica. It is a slender evergreen tree found in many parts of India such as Western Ghats, konkana region, north canara, south canara, Coorg etc. The seeds contain around 45.5% of the oil. The properties of methyl esters of *Garcinia indica* have encouraged it to be used as a potential source for biodiesel production [86].

5.3.1.6. Azadirachta indica (neem). Neem tree is found in many parts of India and Bangladesh. Neem seeds contain around 30% of oil [87]. The oil is light brown in color. It is found to be useful in cosmetic and pharmaceutical industries as well [88]. The esters of neem oil can be used as an alternative fuel for diesel engines to avoid the food and fuel conflict [89].

5.3.1.7. Nicotiana tabacum L. (tobacco). Tobacco seed oil is a by-product of tobacco leaf production. Tobacco cultivators can give an oil yield of 33% to 40% of the mass of the seeds [90]. The fuel properties of biodiesel obtained from tobacco oil were well within the limit set by latest American (ASTM D 6751-02) and European (DIN EN 14214) standards [91].

5.3.1.8. Moringa oleifera (moringa). Moringa is most widely known and utilized in sub-Himalayan regions of northwest India, Africa, Arabia, and Southeast Asia. The cetane number and oxidative stability of moringa are found to be higher than those of other biodiesel fuels [92]. The methyl esters of *Moringa oleifera* could be used in diesel engines, mainly as a mixture to petrodiesel [93].

5.3.1.9. Rubber seeds oil. Rubber seeds contain 40–50% of oil [94]. The maximum yield of oil obtained was 49% [95]. All fuel properties of biodiesel from rubber seeds oil were within the range of standards including the viscosity, flash point, calorific value etc. [96]. The highest conversion efficiency (96.9%) was seen when a limestone-based catalyst was used in the transesterification process to produce biodiesel from high free fatty acid contents of rubber seeds oil [97].

5.3.1.10. Calophyllum inophyllum L. (Polanga). *Calophyllum inophyllum* is available in coastal regions of India, Sri Lanka, East Africa, Australia and Southern Asia [98]. The ester yield was found to be 98.92% and the fuel properties of the blends of *Calophyllum inophyllum* were within the limit set by ASTM standards [99]. It was reported as an excellent feedstock for biodiesel production [98].

5.3.1.11. Sterculia feotida L.. *Sterculia feotida* is native to east Africa, Australia, Myanmar, Sri Lanka and to some extent India. The fuel properties of *Sterculia foetida* methyl esters were within the range of ASTM and EN specifications, except oxidative stability and pour points [100].

5.3.1.12. Ceiba pentandra. *Ceiba pentandra* which is commonly known as kapok is found mainly in Southeast Asia and some parts of India. Its draught-resistant tree grows naturally in humid or semi-humid regions. The blends of biodiesel from *Ceiba pentandra* and diesel showed a remarkable improvement in all fuel properties in general and oxidation stability in particular [101]. The production of biodiesel from *Ceiba pentandra* could add value to this underutilized feedstock [48]. It has also been reported that *Ceiba pentandra* could be used as a feedstock for bioethanol production as well, apart from being used as biodiesel feedstock [102].

5.3.1.13. Rice bran. Rice bran oil which is a potential source for biodiesel production is a by-product of rice milling [103]. The application of two-step transesterification resulted in a good quality biodiesel with acceptable properties compared to the ASTM D6751-02 and DIN V51606 standards [104]. However, high yield could be obtained in shorter period with the application of two-step in situ transesterification process [105].

There are some other non-edible feedstocks available, on which extensive research is being carried out. They are *Cerbera odollam* (Sea mango), *Sapindus mukorossi* (Soapnut), *Thevettia peruviana* (yellow oleander), *Crambe abyssinica* (Hochst), *Aleutites fordii* (Tung), *Sapium sebiferum* (Linn), Roxb (Chinese tallow), *M. azedarach* (syringe), *Putranjiva roxburghii* (Lucky bean tree), *Ricinus communis* (Castor), *Pachira glabra*, *Euphorbia lathyris* L., *Simmondsia chinensis* (Jojoba), *Hibiscus sabdariffa* L. (Roselle), *Guizotia abyssinica*, *Argemone mexicana* L., *Croton megalocarpus* etc. [66,106].

5.4. Fuel properties of biodiesel from non-edible oils

The fuel properties of biodiesel produced from any feedstock vary according to the fatty acid composition of that respective feedstock. The fuel properties of biodiesel are generally expected to be comparable to diesel fuel in order to run the engine successfully without any expensive modifications. These properties include flash point, kinematic viscosity, higher calorific value, oxidation stability, density and cold flow properties. Table 2 illustrates some of the main fuel properties of biodiesel produced from different non-edible feedstocks along with the acceptable limit set by ASTM standards. Among all the properties listed in Table 2, cold flow properties (pour point, cloud point and cold flow plug point CFPP), oxidation stability and kinematic viscosity are among the most important properties which deserve the most attention. Based on these properties it will be decided whether the biodiesel produced could be used in an engine during cold climatic conditions or not. This is because currently European countries are larger consumers of biodiesel [107]. Similarly viscosity of any oil indicates the resistance of a material to flow. It therefore affects the operation of the entire fuel supply system mainly the fuel injection and spray atomization, particularly at lower temperatures [42,66,108]. Oxidation stability is one more important property which describes the degradation tendency of biodiesel and is of great importance in the smooth running of engine parts [109].

5.5. Performance and emissions of biodiesel from non-edible oils

The demand for combustion engines is continuously growing. On one side the customer wants more power and torque and on the other side one cannot lose sight of fuel economy and increasingly stringent emission laws. The main findings of previous literature on the performance of biodiesel fueled internal combustion engine showed that biodiesel has comparable power, brake-specific fuel consumption and brake thermal efficiency [119]. However, the formation of oxides of nitrogen is a matter of concern [120]. Table 3 shows a summary of performance and emission tests on engines fueled by biodiesel prepared from non-edible oils.

6. Emerging technologies

Biodiesel is conventionally produced by homogeneous, heterogeneous, and enzymatic catalyzed processes as well as by supercritical technology as described in the previous chapter. However, all these processes have some limitations, such as waste water generation [138] and high energy consumption [139]. In this context, the following methods appear to be suitable candidates to produce biodiesel in the future because of their ability to overcome limitations encountered by conventional production methods. The conclusions drawn by these methods are described in Table 4. Selection of the production method depends on several

Table 2
Fuel properties of biodiesel from different non-edible oil resources [35,96,110–118].

Properties	Non-edible oils									
	Jatropha Curcas	*Pongamia Pinnata*	*Madhuca Indica*	*Azadirachta indica*	*Moringa oleifera*	*Calophyllum inophyllum*	*Sterculia foetida*	Rice bran	Rubber seed	ASTM D6751-08 standards
Viscosity at 40 °C (mm^2/s)	4.723	4.2	5.10	5.213	5.0735	5.5377	6.3717	3.522	3.89	1.9–6.0
Density at 40 °C (g/cm^3)	0.8642	0.860	0.850	0.8845	0.8597	0.8776	0.8776	–	–	–
Oxidation stability (h at 110 °C)	3.02	2.54	–	7.1	12.64	6.12	1.46	1.70	8.54	Min. 3 h
CFPP (°C)	–	−7	6	11	18	11	2	0	0	–
Cloud point (°C)	3	−1	4	14.4	21	12	1	−10	3.2	–
Pour point (°C)	3	−6	–	2	19	13	2	−11	−2	–
Flash point (°C)	182.5	180	129	76	176	162.2	130.5	169	152	Min. 130
Higher calorific value (kJ/kg)	40,536	40,750	36,914	39,810	40,115	39,513	40,001	38,853	39,700	–

Table 3
Test results of biodiesel (non-edible oils) fueled engines.

Biodiesel	Operating conditions	Performance	Emissions	Ref.
Jatropha Curcas	Full load-variable speed	B10 gave reduced fuel consumption with complete combustion compared to other biodiesel blends	Reduced exhaust emissions except NO_x	[115,121]
Pongamia Pinnata	Gradually variable load constant speed	3–5% Lower brake thermal efficiency for different blends compared to diesel	Reduced unburned hydrocarbon, CO, CO_2 with increased NOx than diesel	[122,123]
Madhuca Indica	Gradually variable load constant speed	B20 resulted slightly better in thermal efficiency than diesel	Reduced hydrocarbon, CO with increased NOx than diesel	[124]
			However, 4% lesser NO_x is reported by Saravanan et al. compared to diesel	[125]
Azadirachta indica	Variable load Constant speed	Brake-specific fuel consumption and thermal efficiency was found to be higher than mineral diesel	Reduced hydrocarbon, CO with increased NO_x than diesel	[126]
Moringa oleifera	Variable speed and full load condition	Reduced brake power with increased fuel consumption for B10 and B20 than diesel	Reduced hydrocarbon, CO with slightly increased NO_x than diesel	[127,128]
Calophyllum inophyllum	Variable speed and full load condition	Higher thermal efficiency and lower specific fuel consumption and exhaust temperature than diesel for B10	Reduced CO and smoke with slight increase in NO_x	[99]
	High idling conditions	Negligible fuel consumption increment compared to diesel	CO and HC were lower, with higher NO_x emissions	[129]
Sterculia foetida	Variable load Constant speed	Power output and fuel consumption were almost same for low biodiesel blend and diesel	Low smoke and CO for low biodiesel concentrated blends. However, 4% reduction in NO_x for B20 was seen	[130]
		B40 blend showed 2.13% more thermal efficiency than diesel at full load	11% Reduction in NO_x for B20 7.4% increment for B40 at full load. Reduction in HC and smoke for B40.	[131]
Ceiba pentandra	Variable speed and full throttle condition	B10 resulted in the best engine torque, brake power and fuel consumption than diesel at 1900 rpm with full throttle	CO, HC and smoke capacity lower compared to diesel except for CO_2 and NO_x	[132]
	Constant speed variable load condition	B25 claimed 4% increase in thermal efficiency than conventional diesel	Comparable emissions of HC, CO, NO_x and smoke with diesel	[133]
Rice bran	Constant speed variable load condition	B20 exhibited marginal fuel consumption difference compared to diesel	Lower smoke and higher NO_x were reported	[134]
Castor oil	Constant speed variable load condition	Increased thermal efficiency with lower fuel consumption for lower biodiesel blends	NOx emissions were same as that of diesel for low loads. Slightly higher NO_x for full load condition	[135,136]
Cotton oil	Variable speed and full throttle condition	No significant differences in performance of B5, B20 and diesel fuel	Lesser CO was reported for all blends. NO_x was found to be less for all blends except B5	[137]

points such as the quality of vegetable oil, type of process desired, quality of raw material, availability and type of oil. However, some of them might have some a promising future than the others based on the outgoing research that is being done daily.

6.1. Low temperature conversion (LTC) process

The low temperature conversion (LTC) is basically a pyrolytic process [140–143]. It has been applied to various biomasses of urban, industrial and agricultural origin to transform them into potential biofuel products [144–149]. LTC is a process that involves only thermal decomposition and does not use any kind of solvent or chemical reagents as utilized by other conventional methods for the production of biodiesel. The other available methods for producing alternative fuels are more sophisticated and complicated relative to the instruments required and reaction conditions. Figueiredo et al. [150] reported an additive produced from castor oil using the LTC process that can be blended with diesel. They concluded that castor seeds could be considered as useful and renewable source of pyrolysis oil with high percentage of pyrolysis oil fraction (50%). It is also important to note that no organic solvents, no reagents and very simple assemblies were used in the LTC process.

6.2. Hydrothermal conversion (HTC) process

Hydrothermal conversion (HTC) process is a very promising method to convert biomass into biofuels [151]. It is a thermochemical process in which biomass is depolymerized to gaseous, aqueous, bio-oil (or bio-crude) and solid by-products in a heated, pressurized and oxygen-free reactor in the presence of water for 5–15 min. This process is conducted at lower temperatures and does not require feedstock drying. HTC bio-oil is found to be suitable as a fuel in stationary diesel engines, burners, boilers and turbines [152]. It could be upgraded further to liquids similar in properties to those of diesel and jet fuels via hydrodeoxygenation [43]. Furthermore, HTC oils typically have much lower oxygen and moisture contents, higher hydrogen content, and consequently higher calorific value than fast pyrolysis oils [153].

The optimum operating conditions for biofuel production from corncobs HTC and the interaction effects between these factors have been investigated by Gan et al. [154]. They concluded that

Table 4
Summary of emerging technologies.

Methods	Biomass/feedstock	Operating conditions	Conclusions drawn	Ref.
Low temperature conversion (LTC) process	Rice straw	Pyrolysis temperature of 693 K	Maximum yield of 10% with higher calorific value 42.79 MJ/kg with viscosity and density lower than other biofuels	[178]
	Castor seeds	Pyrolysis temperature of 653 K	Maximum yield of 50% with higher calorific value 35.656 MJ/kg	[150]
	Sugarcane bagasse	Pyrolysis temperature of 623 K	Maximum yield of 18%. Bio yield could be upgraded by acid hydrolysis	[179]
Hydrothermal conversion (HTC) process	Soybean oil, jatropha oil, and tung oil	Temperature range of 450–475 °C and pressure of 210 bar	Yield ranging from 40% to 52% were reported.	[180]
	Big bluestem	Temperature of 280 °C and pressure of 100 psi	Maximum yield of 27.2% was reported	[181]
	Corncobs	Temperature of 280 °C and pressure of 100 psi	Maximum yield of 41.38% was predicted	[154]
Hydrothermal liquefaction (HTL) process	Cornelian cherry stones	Temperature of 200–300 °C	The highest yield of 28% at both 250 and 300 °C. The higher calorific values for light and heavy bio-oil are 23.86 and 28.35 MJ/kg	[182]
	Woody eucalyptus	Temperature of 150–300 °C	The highest yield of oil obtained with paper regeneration wastewater as solvent	[183]
	Rice straw	Temperature of 300 °C	The highest heavy oil yield of 21.62% for 30 min of hydrothermal liquefaction	[184]
Catalytic hydrodeoxygenation (HDO)	Switchgrass, *Eucalyptus benthamii* pyrolized oil	At a temperature of 320 °C under 2100 psi H_2 atmosphere for 4 h of reaction	Switchgrass bio-oil exhibited in terms of H2 consumption, deoxygenation efficiency	[185]
	Pine sawdust pyrolized oil	At a temperature of 100 °C under 3 MPa H2 atmosphere for 2 h of reaction	The calorific value of raw bio-oil increased from 13.96 MJ/kg to 14.09 MJ/kg with higher contents of carbon and hydrogen	[186]
	Pine sawdust pyrolized oil	Step 1: To overcome coke formation by Ru/C as catalyst at 300 °C, 10 MPa Step 2: Conventional hydrogenation setup at 400 °C, 13 MPa by $NiMo/Al_2O_3$ as catalyst	Oxygen content decreased from 48% to 0.5% and calorific value increased from 17 MJ/kg to 46 MJ/kg	[187]
Membrane biodiesel production and refining technology	Soybean oil	80 °C of reaction temperature, 0.27 g/mL of catalyst amount and 4.15 mL/min velocity at membrane pressure of 80 kPa	Highest yield of 84.1% with many fuel properties within EN14214 standard	[188]
	Soybean oil, canola, palm oil, yellow grease, brown grease	80 °C of reaction temperature, pressure range of 37.9–43.1 kPa	Esters form each feedstock including the low-grade lipids met the ASTM D6751 standard	[189]
	Soybean oil	70 °C of reaction temperature, 0.531 g/cm^3 of catalyst amount and 3.16 mL/min velocity at membrane pressure of 50 kPa	The highest biodiesel yielding rate of 0.1820 g/min was reported	[190]

based on RSM data and prediction models, higher bio-oil yield and carbon recovery could be achieved at low temperature and short retention time.

6.3. Hydrothermal liquefaction (HTL) process

Hydrothermal liquefaction (HTL) is a process in which biomass is converted in hot compressed water to a liquid bio-crude. The processing temperature and pressure are between 200 and 350 °C and 15 and 20 MPa, respectively [155]. These conditions are sufficient to break the complex molecules into desired oily compounds.

Brown and Elliott [156] recently reviewed the early work in hydrothermal processing of wet biomass for both liquid and gas production. Recent reports in literature that have described HTL and its application to algae have been primarily related to batch reactor tests [157]. There have been reports of continuous flow reactor tests for hydrothermal gasification of algae, both subcritical liquid phase [158] and super-critical vapor phase [159]. Recently algae biomass has received a very high level of interest among many researchers as a renewable biomass resource for biofuels production because of their rapid photosynthetic growth rates and high lipid content [160]. The primary focus has been on the recovery of the fatty acid triglycerides produced by the algae as a feedstock for biodiesel production. Elliott et al. [161] reliably processed the algae feedstocks with high slurry concentrations. They achieved high yield of a bio-crude product from whole algae.

6.4. Catalytic hydrodeoxygenation (HDO)

In the HDO process, the main concern is to upgrade the biomass-derived oil by removing the oxygen contents present in the feedstock as water. In addition to this, it also removes sulfur and nitrogen present in the fuel eliminating the chances of the formation of oxides of sulfur and nitrogen [162]. The process includes the treatment of oil at high pressures and moderate temperatures over a heterogeneous catalyst. The use of vegetable oils, mainly non-edible vegetable oils, as feedstocks is highly favorable for this process because their hydrocarbon content is in the same range as that of fossil fuels such as kerosene and diesel. A study by Prasad et al. [163] tried to explain the catalytic hydrodeoxygenation reaction along with the formation of by-products. The chemistry of the reaction and the formation of products purely depend on the catalyst being used in the reaction [164]. The reaction takes place with simple hydrodeoxygenation via an adsorbed enol intermediate and the product is a hydrocarbon fuel with water and propane as the by-products.

The hydrocarbon fuel produced by this hydrodeoxygenation method is characterized by its improved properties compared to conventional petroleum-based fuels. This biofuel exhibits a higher

cetane number. However, the n-paraffinic fuel has poor cold flow properties. To improve these low-temperature properties, the n-paraffin is isomerized to isoparaffin. During the isomerization, the normal paraffin with its high freezing point and outstanding cetane number can be converted to isoparaffin, which has a far lower freezing point but retains a high cetane number [165,166]. Mohammad et al. [167] concluded that hydrodeoxygenation of vegetable oil is a promising route to the production of future fuels from the non-edible feedstocks.

6.5. Membrane biodiesel production and refining technology

Membrane processes for the production and refining of biodiesel are being increasingly reported. Membrane technology has attracted the interest of researchers for its ability to provide high-quality biodiesel and its remarkable yield as well [168–170]. Conventionally biodiesel has been produced by employing batch reactors, continuous stirred tank reactors (CSTR) and plug flow reactors. However, membrane reactor is found to be suitable for biodiesel production due to its ability to restrict the passage of impurities into final biodiesel product [171]. This restriction of impurities helps in obtaining quality biodiesel from the feedstocks. The impurities, mainly the unreacted triglycerides should be removed after the completion of transesterification reaction [172,173]. Biodiesel produced using membrane reactors contains impurities such as glycerol, residual catalyst and excess alcohol, which need removal. The removal of these impurities is generally done by conventional separation and purification techniques which consume a large amount of water, high-energy consumption, time wasting and treatment of wastewater [174,175]. However, this problem could be solved by employing organic/inorganic separative membranes for cleaning the crude biodiesel. Furthermore, organic/inorganic separative membranes have many advantages as they consume low energy, are safer and simple in operation, eliminate wastewater treatment, have easy change of scale, higher mechanical, thermal and chemical stability, and resistance to corrosion [176].

Atadashi et al. [177] concluded that membrane technology could produce a high-quality biodiesel. Furthermore, they reported that properties of biodiesel from the membrane technology process were in agreement with the ASTM standard specification.

7. Conclusion

Most of the biodiesel fuels are produced from edible oils, whose large-scale consumption is leading to price rise and shortage of food supplies. Hence, the focus is on looking into different non-edible feedstocks for biodiesel production. Moreover, non-edible feedstocks could be potential resources due to their favorable fuel properties, performance and emission characteristics. There are several reported methods for biodiesel production. However, still conventional technologies are being implemented on large-scale production. Emerging technologies can make the energy resources more efficient and eco-friendly. Therefore, the concepts of membrane biodiesel production and thermal conversion processes could be extended to non-edible feedstocks. There is a scope to improve fuel properties of biodiesel from non-edible feedstocks by methods such as catalytic hydrodeoxygenation. Though the discussed technologies are applied to selected feedstocks, nevertheless the same could be tried for other feedstocks and could be investigated for further upgradation.

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